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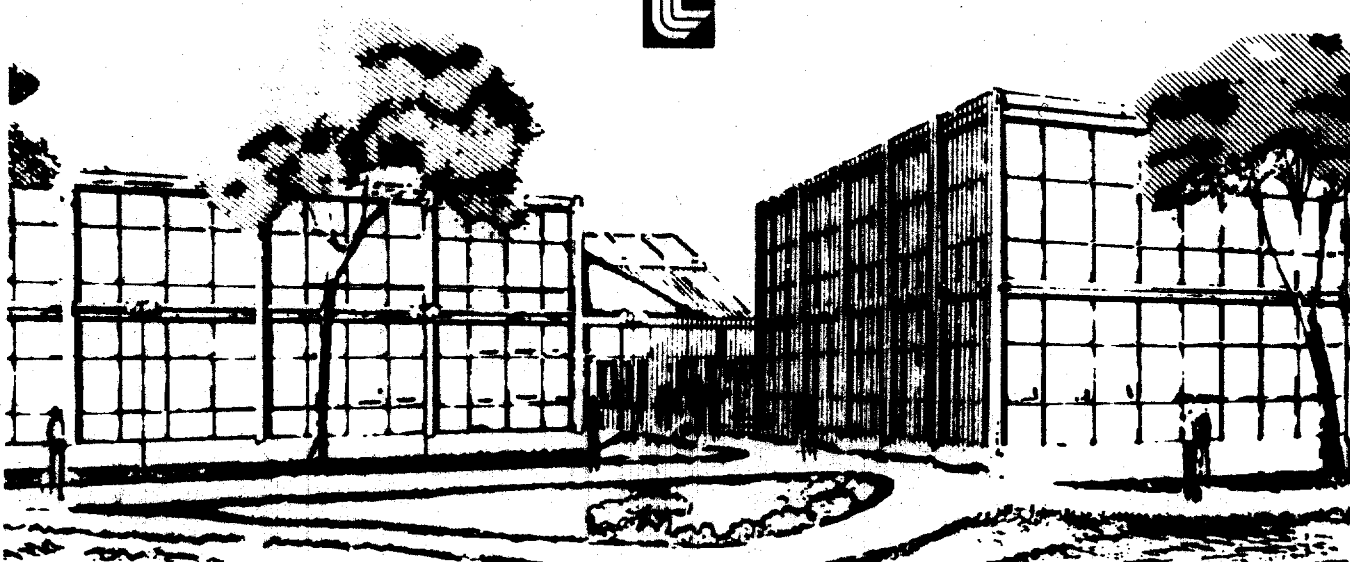

K-L AND L-K VACANCY SHARING IN ION-ATOM COLLISIONS

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Introduction

The molecular model[1] has been very successful in explaining the production of atomic vacancies in low energy ion-atom collisions. One area of active investigation involves the sharing of inner-shell vacancies between two collision partners. The sharing results when a vacancy, which has been produced at some smaller internuclear distance, is transferred from one molecular orbital (MO) to another during the separation of the two collision partners. K-shell vacancy sharing in near symmetric collisions due to radial coupling between the 1sσ and 2pσ MOs has been studied extensively.[2] Meyerhof[3] derived a simple formula, using a parameterization of the Demkov formalism,[4] which was very successful in explaining a large body of data on K-K vacancy sharing. In this paper I will summarize the current situation involving sharing of K and L vacancies in highly asymmetric collisions ($Z_1/Z_2 \geq 2$).

Theoretical

Before discussing the experimental data some introduction into the theoretical models available for calculation of vacancy sharing is needed. The simplest approach is to assume that only the two states involved in the sharing need be considered. One assumes two orthonormal states with the same symmetry $|\phi_i^0\rangle$, which are approximate solutions to the Hamiltonian H. The eigenstate Ψ of H is assumed to have the form $|\Psi\rangle = c_1|\phi_1^0\rangle + c_2|\phi_2^0\rangle$. Substitution into the Schrodinger equation yields

$$c_1(H_{11}-E) + c_2H_{12} = 0$$

$$c_1H_{21} + c_2(H_{22}-E) = 0$$

where

$$H_{ij} = \langle\phi_i|H|\phi_j\rangle \quad . \tag{1}$$

This yields two solutions which are designated $|\psi_1\rangle$ and $|\psi_2\rangle$ with energy eigenvalues

$$E_{1,2} = \frac{1}{2}(H_{11} + H_{22}) + 1/2\sqrt{(H_{11} - H_{22})^2 + 4|H_{12}|^2} \tag{2}$$

The two states, $|\psi_1\rangle$ and $|\psi_2\rangle$, are adiabatic states and cannot cross unless $(H_{11} - H_{22})$ and H_{12} are both zero. The approximate states $|\phi_1^0\rangle$ and $|\phi_2^0\rangle$ pass smoothly through a crossing, R_x (i.e. $H_{11} = H_{22}$) and are called diabatic states. If one defines an angle β, such that

$$\tan\beta = \frac{2H_{12}}{H_{11} - H_{22}} \tag{3}$$

one can show

$$|\Psi_1\rangle = \cos\frac{1}{2}\beta|\phi_1^0\rangle + \sin\frac{1}{2}\beta|\phi_2^0\rangle$$

$$|\Psi_2\rangle = -\sin\frac{1}{2}\beta|\phi_1^0\rangle + \cos\frac{1}{2}\beta|\phi_2^0\rangle \tag{4}$$

special cases are $|H_{11} - H_{22}| \gg |H_{12}|$, $\beta = 0$ $|\Psi_1\rangle = |\phi_1^0\rangle$ and $|\Psi_2\rangle = |\phi_2^0\rangle$. On the contrary $|H_{11} - H_{22}| \ll |H_{12}|$, $\beta = \pi/2$ and $|\Psi_1\rangle = 1/\sqrt{2}(|\phi_1^0\rangle + |\phi_2^0\rangle)$ and $|\Psi_2\rangle = 1/\sqrt{2}(-|\phi_1^0\rangle + |\phi_2^0\rangle)$.

The most general solution to the problem is the exponential model of Nikitin.[5] This is found by setting

$$H_{12} = -\frac{1}{2}C\exp(-\alpha R) \quad \text{and}$$

$$H_{11} - H_{22} = \Delta\varepsilon - D\exp(-\alpha R) \quad . \tag{5}$$

where $\Delta\varepsilon$, α, C, and D are adjustable parameters. It is convenient to redefine the adjustable parameters in terms of the angle defined by Eq. (3) by noticing that as $R \to 0$ $D\exp(-\alpha R) \gg \Delta\varepsilon$ then

$$\tan\beta \to \frac{C}{D} \equiv \tan\theta$$

or

$$c = A\sin\theta \quad D = A\cos\theta \quad . \tag{6}$$

For convenience we set

$$A\exp(-\alpha R_x) = \Delta\varepsilon \tag{7}$$

Finally setting $R = R_x + \Delta R$ and using Eqs. (2), (5), (6), and (7) we can write the energy difference between the two adiabatic states in terms of the adjustable parameters

$$\Delta E = E_1 - E_2 = \Delta\varepsilon\left\{1 - 2\cos\theta\exp[-\alpha\Delta R] + \exp[-2\alpha\Delta R]\right\}^{1/2} \tag{8}$$

Equation (8) has several interesting properties, for $\theta < \pi/2$ ΔE exhibits a minimum, for $\theta \geq \pi/2$ the two adiabatic states actually diverge. By examining Eq. (8) the physical interpretation of the adjustable parameters is clear, $\Delta E \to \Delta\varepsilon$ as $R \to \infty$, thus $\Delta\varepsilon$ is the energy difference between the atomic states, R_x is the crossing radius, $1/\alpha$ is the width of the region about R_x where the coupling takes place and θ is an adjustable parameter called the Nikitin angle whose physical interpretation is defined in Eqs. (4) and (6). The adjustable parameters ($\Delta\varepsilon$, α, R_x, θ) can be determined by a fit to the energy difference between two adiabatic energy curves such as those calculated in a Hartree-Fock approximation. Nikitin calculated the coupling probability P_{12} in terms of the adjustable parameters to be

$$P_{12} = \frac{\exp[2\pi\Delta\varepsilon\ \cos^2(\theta/2)/\alpha v]-1}{\exp[2\pi\Delta\varepsilon/\alpha v]-1} \qquad (9)$$

The sharing ratio R is simply

$$R = \frac{P_{12}}{1-P_{12}} \qquad (10)$$

There are two important limiting cases to the Nikitin formalism. If we set $(\Delta\varepsilon,\alpha,\theta) = (I_H-I_L, (\sqrt{I_H} + \sqrt{I_L})/\sqrt{2},\pi/2)$ then P_{12} and R reduce to the well known values as derived by Meyerhof, i.e.

$$R = e^{-\pi\sqrt{2}(I_H^{1/2} - I_L^{1/2})/v} \quad . \qquad (11)$$

This represents the case where the energy difference has no minimum but the levels remain parallel for the maximum range of internuclear distances. The second limiting case is for small values of the Nikitin angle, θ, i.e. $\theta \ll \pi/2$. In this case Eq. (9) reduces to the well known expression for the Landau-Zener formula

$$P_{12} = \exp -2\pi H_{12}^2 /v\frac{d}{dR} (H_{11} - H_{22}) \Big|_{R = R_x} \qquad (12)$$

for the coupling probability between two adiabadic molecular levels which exhibit a strong minimum in the energy difference, i.e., an avoided crossing. The Landau-Zener (LZ) and the Meyerhof-Demkov (MD) formulas being two different limiting cases exhibit different characteristics. In the MD formalism P_{12} has values between 0 and .5, whereas in the LZ cases the values range between 0 and 1.0. Thus diabatic behavior ($P_{12} \rightarrow 1$) for the molecular levels is excluded in the MD picture but not in the LZ model.

K-L and L-K Vacancy Sharing

Vacancy sharing is a well-suited method for studying the coupling probability P_{12} described above. Since the primary vacancy is produced at very small internuclear distances, the vacancy sharing takes place in a single passage thru the interaction region as the collision partners separate. In addition since inner shells are involved the number of molecular levels involved in the coupling is small, thus the two-state approximation might be expected to apply for some cases. As mentioned earlier, KK sharing has been studied extensively and in general the MD formalism works quite well.[2,6] However, K-L vacancy sharing represents a fundamentally different system to K-K sharing. In Fig. 1 we illustrate vacancy sharing for three different cases which we call KK, LK, and KL sharing. In each case the first letter designates which atomic level the primary vacancy is correlated to in the adiabatic diagrams. It is clear from the figure that this is the level of least atomic binding energy. The biggest point to be gleaned from the figure is that in the highly asymmetric collision, i.e. KL and LK sharing cases, the 1s level, due to polarization and Stark effects, induced by the strong electric field of the heavy collision partner rapidly decreases as R decreases. In the case of LK sharing, the relevant levels (4σ and 2σ) actually diverge. In the case of KL sharing the strong decrease

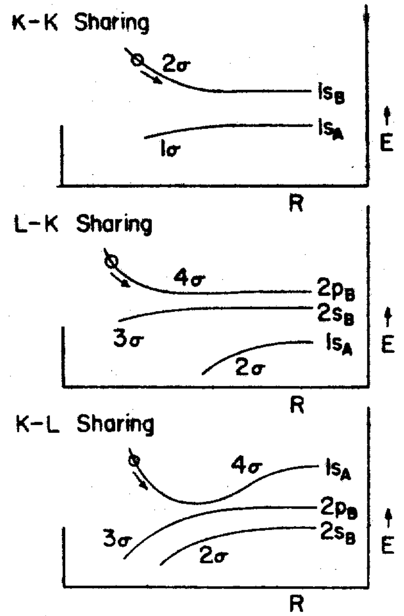

Figure 1. Molecular orbital curves demonstrating differences between K-K, L-K and K-L vacancy sharing.

in energy produces an apparent avoided crossing between the 3σ and 4σ levels. In the language of the Nikitin formalism LK sharing corresponds to systems where $\theta > \pi/2$ and KL sharing corresponds to systems where $\theta < \pi/2$. In the case of KK sharing, the levels remain parallel during much of the collision correlating to the case where $\theta \simeq \pi/2$.

Experimental Data

The Nikitin formalism has been applied to the vacancy sharing problem. Boving[6] first applied the fitting procedure to the case of K-K sharing to explain small deviations from the MD formula seen in low Z collision systems. Woerlee[7] et al. first observed the avoided crossing in K-L sharing and successfully applied the Nikitin formalism to K-L sharing in Ne-Kr collisions. Other authors[8-9] have measured K-L and L-K vacancy sharing, but did not have MO calculations available for the collision systems studied, thus they had limited success in applying the Nikitin formalism. In Figs. 2 and 3 I show the results of some recent measurements and calculations obtained at Livermore[10] which typify the available measurements. In Fig. 2 we consider K-L vacancy sharing in Cℓ → Xe collisions. The insert shows the calculated energy difference $\Delta\varepsilon(3\sigma - 4\sigma)$ obtained from the VSM of Eichler and Wille.[11] The solid line shows a fit to the energy difference using Eq. (8). From the fit we obtain the parameters in a.u. $(\Delta\varepsilon, \alpha, R_x, \theta) = (67.0, 7.0, .243, 25°)$ which are then used to calculate the Nikitin vacancy sharing ratios which are indicated in the figure. The values for MD, also shown in the figure, are substantially

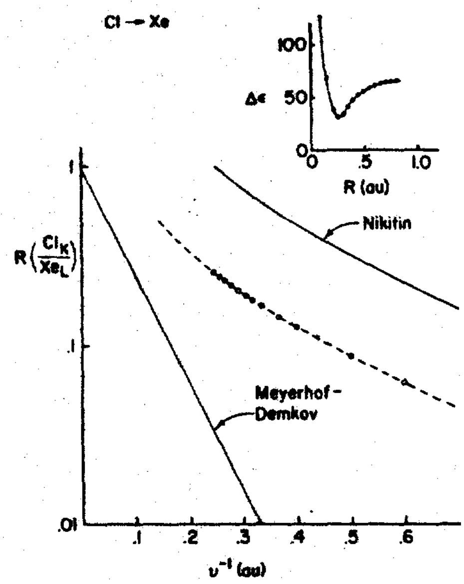

Figure 2. Typical case for K-L vacancy sharing. $R[\sigma_x(X_{eL})/\sigma_x(C\ell K)]$ vs $1/v$. Insert shows calculated energy difference $\Delta\varepsilon(3\sigma\text{-}4\sigma)$ plotted as a function of internuclear distance, R. See text.

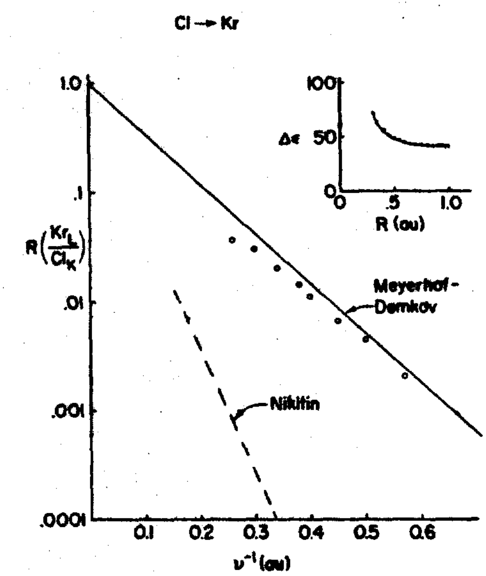

Figure 3. Typical case for L-K vacancy sharing. $R[\sigma_x(C\ell K)/\sigma(Kr L)]$ vs $1/v$. Insert shows calculated energy difference $\Delta\varepsilon(2\sigma\text{-}4\sigma)$ plotted as a function of internuclear distance, R. See text.

smaller as one would expect due to the strong minimum in the $\Delta\varepsilon$ curve. The data in the figure indicate the ratio of x-ray production cross sections which should be corrected for difference in fluorescence yields. It is clear from the figure that the slope of the data agrees very well with the Nikitin predictions. The dashed line in the figure shows the Nikitin predictions normalized to the data at one point. Similar behavior for K-L vacancy sharing in Ne-Kr systems has been previously reported.[7]

The situation for L-K vacancy sharing is very different. In Fig. 3 the data for $C\ell \rightarrow Kr$ collisions are presented. The insert curve shows $\Delta\varepsilon(2\sigma\text{-}4\sigma)$ has no minimum and actually diverges as R decreases. Again the solid line shows the fit of Eq. (8) which yields the parameters $(\Delta\varepsilon, \alpha, R_x, \theta) \rightarrow (42.17, 6.6, .33, 110°)$. The predicted vacancy sharing ratios, R, for the Nikitin formalism are substantially smaller than MD as expected. However the data, which have not been corrected for fluorescence yields agree very well with the MD predictions. The data suggest that coupling at R values greater than R_x where $\Delta\varepsilon$ is constant dominate the vacancy sharing and the application of MD in this region works reasonably well. Note in the analysis of L-K sharing we have neglected the 3σ level. A more rigorous theoretical treatment would be valuable in justifying this point.

It is clear from the above discussion that K-L vacancy sharing is a tool for studying molecular orbital curves. In Fig. 4, a comparison of $\Delta\varepsilon(3\sigma\text{-}4\sigma)$ for B-Ar collisions calculated using the VSM[11] code and a Hartree-Fock (HF) code.[12] The two curves are quite different. In Fig. 5 a comparison of the experimental data with the Nikitin model calculated with the HF curves shows good agreement indicating the HF values are more reasonable.

The final point to be made concerns the new correlation rules.[14] A new correlation rule is obtained at an avoided crossing when $P_{12} > 1/2$, i.e. $R > 1$. Indeed in K-L vacancy sharing it is possible to apply the Nikitin formalism to collision systems with strong minimum in the $\Delta\varepsilon$ vs R curves and calculate R values in excess of 1. However no experimental data have been obtained which indicate values of R greater than 1. We have considered two systems $F \rightarrow Kr$ and $Ar \rightarrow Sn$. The values of R calculated from the Nikitin formalism in the regions where experimental data[9,10] exist clearly predict values in excess of unity. However the data within experimental error give a constant value of 1.0. This suggests that the Nikitin model, and thus the LZ model, break down for high coupling probabilities of $P_{12} > .5$. If this is indeed the case the arguments which were used to predict new correlation rules must be reconsidered.

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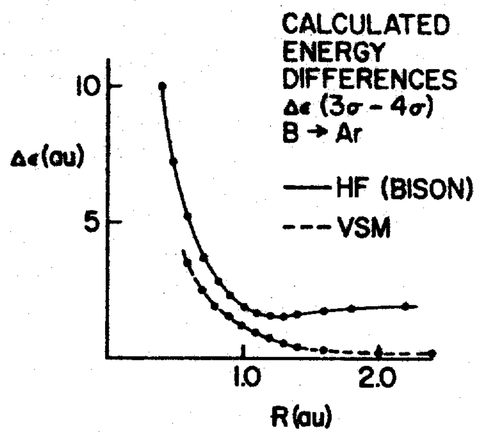

Figure 4. *Calculated energy difference Δε(3σ-4σ) plotted as a function of R for two different types of calculations.*

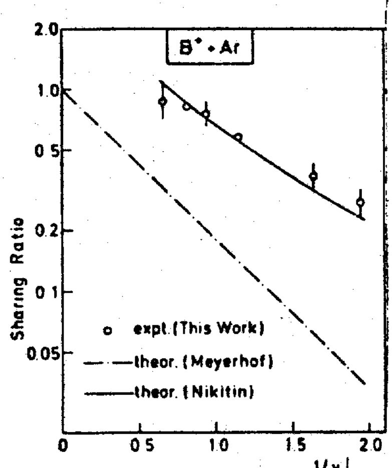

Figure 5. *Experimental data for B-Ar collisions compared to two different theoretical models.*

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